

Orientational Effect of Aryl Groups in Aryl Selenides: How Can ^1H and ^{13}C NMR Chemical Shifts Clarify the Effect?

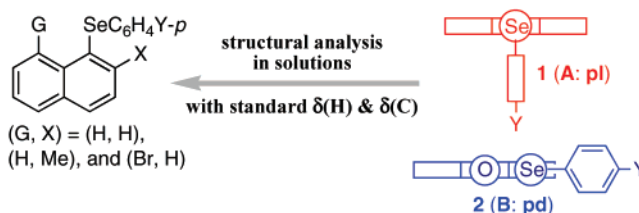
Satoko Hayashi, Kentaro Yamane, and Waro Nakanishi*

Department of Material Science and Chemistry, Faculty of Systems Engineering, Wakayama University,
930 Sakaedani, Wakayama 640-8510, Japan

nakanisi@sys.wakayama-u.ac.jp

Received May 11, 2007

Proposal of $\delta(\text{C}\&\text{H})$ for standards of analysis in solutions



Two sets of $\delta(\text{H})$ and $\delta(\text{C})$ are proposed by employing 9-(arylselanyl)anthracenes [9-(*p*- $\text{YC}_6\text{H}_4\text{Se}$)Atc: **1**] and 1-(arylselanyl)anthraquinones [1-(*p*- $\text{YC}_6\text{H}_4\text{Se}$)Atq: **2**] with various Y's. Structures of **1** and **2** are (A: **pl**) and (B: **pd**), respectively, for all Y examined in chloroform-*d*. After elucidation of the behavior of $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$, they are applied to determine the structures in chloroform-*d* solutions for 1-(arylselanyl)naphthalenes (**3**), 1-(arylselanyl)-2-methylnaphthalenes (**4**), and 1-(arylselanyl)-8-bromonaphthalenes (**5**). Although the structure of **4** remains in (A: **pl**) in the solutions for all Y examined, that of **5** is (B: **pd**), except for Y = CN and NO₂. On the other hand, **3** is shown to equilibrate between (A: **pl**) and (B: **pd**). Although the contributions of (B: **pd**) and (A: **pl**) are predominant for Y = NMe₂ and NO₂, respectively, the equilibrium constants change from Y to Y in the solutions. The results are supported by the quantum chemical calculations, containing the solvent effect of chloroform. These results demonstrate that $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$, as well as $\delta(\text{Se})$, serve as the practical standards for **pl** and **pd**, respectively, to analyze the structures of *p*- $\text{YC}_6\text{H}_4\text{ZR}$ (Z = Se) in solutions.

Introduction

NMR spectroscopy is an extremely powerful tool to study chemistry.^{1–5} NMR chemical shifts (δ) are widely applied to determine structures^{2–5} and follow reactions.^{1,2} $\delta(\text{H})$ are mainly affected not only by the charge density at the hydrogen in question but also by the anisotropy around the nuclei. $\delta(\text{C})$ seem to behave similarly to $\delta(\text{H})$ at first glance; however, they are essentially determined by the paramagnetic contributions. The hybridization conditions and the charge density at the carbon

in question greatly affect $\delta(\text{C})$. On the other hand, $\delta(\text{Se})$ are sharply sensitive to structural changes of selenium compounds.

* To whom correspondence should be addressed. Tel: +81 73 457 8252. Fax: +81 73 457 8253.

(1) *Organic Selenium Compounds: Their Chemistry and Biology*; Klayman, D. L., Günther, W. H. H., Eds.; Wiley: New York, 1973. *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John-Wiley and Sons: New York, 1986; Vols. 1 and 2. *Organic Selenium Chemistry*; Liotta, D., Ed.; Wiley-Interscience: New York, 1987. *Organoselenium Chemistry, A practical Approach*; Back, T. G., Ed.; Oxford University Press: Oxford, 1999. *Organoselenium Chemistry Modern Developments in Organic Synthesis, Top. Curr. Chem.*; Wirth, T., Ed.; Springer: Berlin, Heidelberg, New York, London, Paris, Tokyo, 2000; Vol. 208.

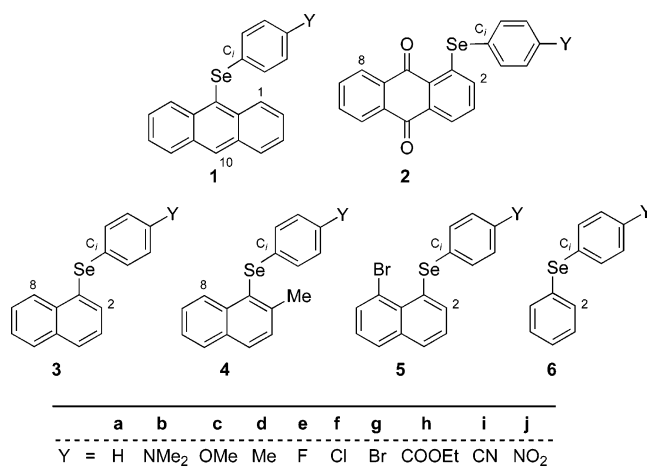
(2) (a) MacFarlane, W.; Wood, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1397–1401. (b) Iwamura, H.; Nakanishi, W. *J. Synth. Org. Chem. Jpn.* **1981**, 39, 795–804. (c) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John-Wiley and Sons: New York, 1986; Vol. 1, Chapter 6. (d) *Compilation of Reported ^{77}Se NMR Chemical Shifts*; Klapotke, T. M., Broschag, M., Eds.; Wiley: New York, 1996. (e) Duddeck, H. *Prog. Nucl. Magn. Reson. Spectrosc.* **1995**, 27, 1–323.

(3) (a) Kalabin, G. A.; Kushnarev, D. F.; Bzesovsky, V. M.; Tschmutova, G. A. *J. Org. Mag. Res.* **1979**, 12, 598–604. (b) Kalabin, G. A.; Kushnarev, D. F.; Mannafov, T. G. *Zh. Org. Khim.* **1980**, 16, 505–512. (c) Mullen, G. P.; Luthra, N. P.; Dunlap, R. B.; Odom, J. D. *J. Org. Chem.* **1985**, 50, 811–816. (d) Nakanishi, W.; Hayashi, S.; Uehara, T. *Eur. J. Org. Chem.* **2001**, 3933–3943.

(4) (a) Hayashi, S.; Nakanishi, W. *J. Org. Chem.* **1999**, 64, 6688–6696. (b) Nakanishi, W.; Hayashi, S.; Yamaguchi, H. *Chem. Lett.* **1996**, 947–948. (c) Nakanishi, W.; Hayashi, S.; Sakaue, A.; Ono, G.; Kawada, Y. *J. Am. Chem. Soc.* **1998**, 120, 3635–3640. (d) Nakanishi, W.; Hayashi, S. *J. Org. Chem.* **2002**, 67, 38–48.

(5) (a) Nakanishi, W.; Hayashi, S. *Chem. Lett.* **1998**, 523–524. (b) Nakanishi, W.; Hayashi, S. *J. Phys. Chem. A* **1999**, 103, 6074–6081.

CHART 1



The paramagnetic terms predominantly contribute to them. $\delta(\text{Se})$ of divalent selenides are well explained by the pre- α , α , β , and γ effects, where the pre- α effect is proposed for the better interpretation of $\delta(\text{Se})$.⁶ The origin of the effects is revealed based on the MO theory.⁶

We often worry about the structures of compounds in solutions, when investigations are carried out in solutions, even if the structures are determined in crystals. The importance of the orientational effect on $\delta(\text{Se})$ of $p\text{-YC}_6\text{H}_4\text{SeR}$ (ArSeR) has been pointed out to determine the structure of ArSeR on the basis of $\delta(\text{Se})$ in solutions.^{5,6} To establish the orientational effect, it is inevitable to fix the structures of $p\text{-YC}_6\text{H}_4$ (Ar) in ArSeR to be the planar (**pl**) or perpendicular (**pd**) orientation for all Y examined, where the $\text{Se}-\text{C}_R$ bond in ArSeR is on the Ar plane in **pl**, and it is perpendicular to the plane in **pd**.⁷⁻⁹ 9-(Arylselanyl)anthracenes [**1**: 9-($p\text{-YC}_6\text{H}_4\text{Se}$)Atc] and 1-(arylselanyl)anthraquinones [**2**: 1-($p\text{-YC}_6\text{H}_4\text{Se}$)Atq] are employed for **pl** and **pd**, respectively, where Y in **1** and **2** is H (**a**), NMe₂ (**b**), OMe (**c**), Me (**d**), F (**e**), Cl (**f**), Br (**g**), COOEt (**h**), CN (**i**), and NO₂ (**j**) (Chart 1).¹⁰ Two sets of $\delta(\text{Se})$ are proposed for **pl** and **pd** of $p\text{-YC}_6\text{H}_4$ (Ar) in ArSeR which are determined based on **1** and **2**, respectively.

The sets of $\delta(\text{Se})$ in **1** [$\delta(\text{Se}: \mathbf{1})$] and $\delta(\text{Se}: \mathbf{2})$ serve as typical ones for **pl** and **pd**, respectively. It must be more useful if $\delta(\text{H})$ and $\delta(\text{C})$ of **1** [$\delta(\text{H}, \text{C}: \mathbf{1})$] and $\delta(\text{H}, \text{C}: \mathbf{2})$ work as the standard of **pl** and **pd**, respectively. It is necessary to clarify the behavior

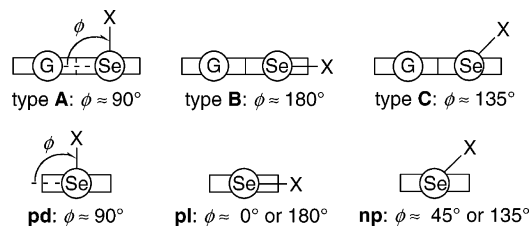
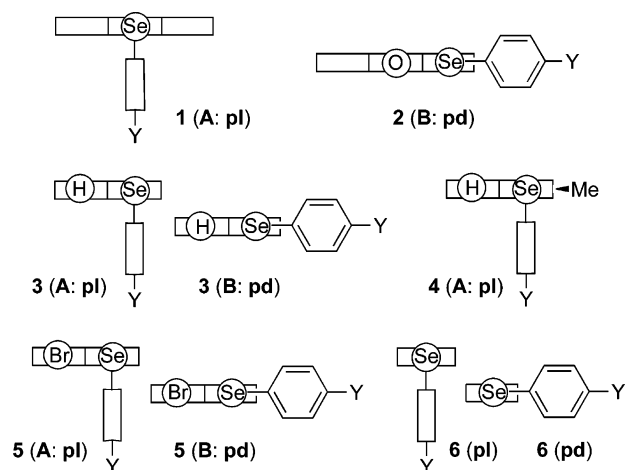
(6) Nakanishi, W.; Hayashi, S.; Shimizu, D.; Hada, M. *Chem.-Eur. J.* **2006**, *12*, 3829–3846; *Chem. Eur. J.* **2007**, *13*, 5282–5293.

(7) Nakanishi, W.; Hayashi, S.; Uehara, T. *J. Phys. Chem. A* **1999**, *103*, 9906–9912.

(8) The nonplanar and nonperpendicular conformer (**np**) is also important in some cases, such as the **CC** conformer in 1,8-(MeZ)₂C₁₀H₆ (Z = S and Se).²²

(9) The importance of relative conformations in the substituent effects between substituents and probe sites is pointed out. See, for example: Bordwen, K.; Grubbs, E. J. *Angular Dependence of Dipolar Substituent Effects*. In *Progress in Physical Organic Chemistry*; Taft, R. W., Ed.; John Wiley & Sons: New York, 1993; Vol. 19, pp 183–224. See also refs cited therein.

(10) A basic set containing substituents of differing relative polar and resonance effects has been suggested: two from NMe₂, OMe, NH₂, two halogens (but not both Cl and Br), Me, H, and two electron-withdrawing groups. From a spectroscopic point of view, to avoid any specific interactions, any d-orbitals, or any mass effect, the following substituents are recommended: Y = NMe₂, OMe, F, Cl, Me, H, and two from CF₃, CN, COY, and NO₂. See: Topsom, R. D. *The Nature and Analysis of Substituent Electronic Effects*. In *Progress in Physical Organic Chemistry*; Taft, R. W., Ed.; John Wiley & Sons: New York, 1976; Vol. 12, pp 1–20.

SCHEME 1. Types A–C in the Naphthalene System and **pd**, **pl**, and **np** in the Benzene SystemSCHEME 2. **1** (A: **pl**) and **2** (B: **pd**), Together with Plausible Structures of **3–6**

of $\delta(\text{H})$ and $\delta(\text{C})$ with the fixed structures, as a first step to establish the relation between the chemical shifts and the orientational effect. Because **1** and **2** are fixed to be **pl** and **pd**, respectively, for all Y examined under the conditions, $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$ can be used in close relation to the structures. By application of $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$ to other ArSeR , it enables us to discuss the structures on the firm basis in relation to the orientational effect.

The notation of type **A** (**A**), type **B** (**B**), and type **C** (**C**) is proposed on the basis of the observed structures of 1-(arylselanyl)naphthalenes [**3**: 1-($p\text{-YC}_6\text{H}_4\text{Se}$)Nap] and the related compounds.^{3d,4,5,7} The notation is applied to the 9-anthracenyl (9-Atc) and 1-anthraquinonyl (1-Atq) groups in **1** and **2**, respectively. The structure of **1** is **A** for 9-Atc and **pl** for Ar, which is denoted by **1** (A: **pl**). That of **2** is **B** for the 1-Atq and **pd** for Ar [**2** (B: **pd**)]. Scheme 1 shows type **A** (**A**), type **B** (**B**), and type **C** (**C**) in the naphthalene system, together with **pd**, **pl**, and **np** (nonplanar and nonperpendicular orientation)⁸ in the benzene system. Scheme 2 illustrates **1** (A: **pl**) and **2** (B: **pd**), together with the plausible structures of **3–6**.

Here, we report the results of investigations on the behavior of $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$ and the applications to the structural determination in solutions for **3**, 1-(arylselanyl)-2-methylnaphthalenes [**4**: 1-($p\text{-YC}_6\text{H}_4\text{Se}$)NapMe-2], and 1-(arylselanyl)-8-bromonaphthalenes [**5**: 1-($p\text{-YC}_6\text{H}_4\text{Se}$)NapBr-8]. Aryl phenyl selenides (**6**: $p\text{-YC}_6\text{H}_4\text{SePh}$) are used as models of **1** and **2**, if necessary. Quantum chemical (QC) calculations are also employed to support the observed results and to analyze the mechanism of the orientational effect.

Results and Discussion

$\delta(\text{H})$ and $\delta(\text{C})$ of **1–5**. Aryl selenides **4** bearing Y = H (**a**), OMe (**c**), Me (**d**), Cl (**f**), Br (**g**), COOEt (**h**), and NO₂ (**j**) were prepared, together with **3**^{3d} having Y = NMe₂ (**b**), F (**e**), and

TABLE 1. Substituent Induced Chemical Shifts (δ_{SCS}) of 1H , ^{13}C , and ^{77}Se Nuclei of Some Selenides

| | NMe ₂ | OMe | Me | H | | F | Cl | Br | CO ₂ Et | CN | NO ₂ |
|------------------------|------------------|--------|--------|-------|-----------------------|--------|--------|--------|--------------------|--------|-----------------|
| | (b) | (c) | (d) | (a) | | (e) | (f) | (g) | (h) | (i) | (j) |
| 1 | | | | | | | | | | | |
| $\delta(H_1)_{SCS}$ | 0.127 | 0.045 | 0.005 | 0.000 | (8.884) ^a | -0.028 | -0.075 | -0.084 | -0.166 | -0.186 | -0.218 |
| $\delta(H_{10})_{SCS}$ | -0.077 | -0.045 | -0.019 | 0.000 | (8.567) ^a | -0.008 | 0.008 | 0.010 | 0.071 | 0.060 | 0.103 |
| $\delta(H_o)_{SCS}$ | 0.084 | 0.044 | -0.068 | 0.000 | (7.057) ^a | 0.005 | -0.073 | -0.157 | -0.017 | -0.028 | -0.007 |
| $\delta(C_i)_{SCS}$ | -8.13 | -3.11 | -1.13 | 0.00 | (126.57) ^a | 1.24 | 2.83 | 3.94 | 13.23 | 14.89 | 17.73 |
| $\delta(Se)_{SCS}$ | -21.0 | -12.2 | -6.6 | 0.0 | (249.0) ^a | -3.6 | 1.5 | 1.6 | 16.2 | 26.2 | 30.3 |
| 2 | | | | | | | | | | | |
| $\delta(H_2)_{SCS}$ | 0.102 | 0.023 | 0.024 | 0.000 | (7.237) ^a | -0.038 | -0.017 | -0.012 | -0.052 | -0.056 | -0.052 |
| $\delta(H_8)_{SCS}$ | 0.024 | 0.022 | 0.013 | 0.000 | (8.352) ^a | 0.005 | 0.011 | 0.010 | 0.016 | 0.011 | 0.018 |
| $\delta(H_o)_{SCS}$ | -0.196 | -0.102 | -0.128 | 0.000 | (7.724) ^a | -0.032 | -0.071 | -0.144 | 0.046 | -0.009 | 0.196 |
| $\delta(C_i)_{SCS}$ | -13.87 | -8.05 | -2.06 | 0.00 | (127.44) ^a | -3.45 | 2.21 | 2.21 | 5.26 | 5.27 | 5.66 |
| $\delta(Se)_{SCS}$ | -19.5 | -15.0 | -8.9 | 0.0 | (512.3) ^a | -10.1 | -7.0 | -6.4 | 0.0 | 8.2 | 2.5 |
| 3 | | | | | | | | | | | |
| $\delta(H_2)_{SCS}$ | -0.467 | -0.277 | -0.108 | 0.000 | (7.776) ^a | -0.101 | 0.003 | 0.021 | 0.096 | 0.113 | 0.125 |
| $\delta(H_8)_{SCS}$ | -0.088 | -0.068 | -0.021 | 0.000 | (8.348) ^a | -0.053 | -0.062 | -0.059 | -0.068 | -0.101 | -0.109 |
| $\delta(C_i)_{SCS}$ | -18.15 | -11.48 | -4.37 | 0.00 | (131.66) ^a | -5.98 | -1.55 | -0.64 | 8.17 | 9.45 | 12.36 |
| $\delta(Se)_{SCS}$ | -17.2 | -6.8 | -4.8 | 0.0 | (361.0) ^a | -5.0 | -1.6 | -1.7 | 7.0 | 13.8 | 18.6 |
| 4 | | | | | | | | | | | |
| $\delta(H_{Me})$ | | 0.005 | 0.001 | 0.000 | (2.706) ^a | | -0.014 | -0.016 | -0.020 | | -0.013 |
| $\delta(H_8)$ | | 0.057 | 0.022 | 0.000 | (8.589) ^a | | -0.060 | -0.069 | -0.123 | | -0.179 |
| $\delta(Se)$ | | -11.5 | -6.2 | 0.0 | (274.6) ^a | | 1.1 | 1.4 | 15.0 | | 29.2 |
| 5 | | | | | | | | | | | |
| $\delta(H_2)_{SCS}$ | | -0.073 | -0.043 | 0.000 | (7.217) ^a | | -0.016 | -0.025 | 0.041 | 0.270 | 0.388 |
| $\delta(Se)_{SCS}$ | | -14.0 | -8.6 | 0.0 | (451.0) ^a | | -6.4 | -5.9 | 2.7 | 13.2 | 13.4 |

^a $\delta(H)_{SCS}$, $\delta(C)_{SCS}$, and $\delta(Se)_{SCS}$ are given for **1–5**, together with $\delta(H)$, $\delta(C)$, and $\delta(Se)$ for **1a–5a** in parentheses, measured in chloroform-*d*.

TABLE 2. Evaluated Atomic Charges (Q_n) on C_i and Se of **6 (pl)** and **6 (pd)**^a

| | Y = NMe ₂ | OMe | Me | H | F | Cl | Br | CO ₂ Me | CN | NO ₂ |
|---------------|----------------------|--------|--------|--------|--------|--------|--------|--------------------|--------|-----------------|
| Q_n | (b) | (c) | (d) | (a) | (e) | (f) | (g) | (h) | (i) | (j) |
| 6 (pl) | | | | | | | | | | |
| $Q_n(C_i)$ | -0.246 | -0.231 | -0.210 | -0.204 | -0.221 | -0.210 | -0.209 | -0.187 | -0.190 | -0.185 |
| $Q_n(Se)$ | 0.381 | 0.387 | 0.392 | 0.396 | 0.398 | 0.404 | 0.405 | 0.415 | 0.424 | 0.435 |
| 6 (pd) | | | | | | | | | | |
| $Q_n(C_i)$ | -0.295 | -0.275 | -0.248 | -0.239 | -0.258 | -0.244 | -0.242 | -0.217 | -0.217 | -0.209 |
| $Q_n(Se)$ | 0.394 | 0.397 | 0.395 | 0.396 | 0.401 | 0.401 | 0.401 | 0.399 | 0.404 | 0.405 |

^a Calculated with the 6-311+G(3df) basis sets for Se and the 6-311+G(3d,2p) basis sets for other nuclei in the Gaussian 03 program.¹⁴

CN (**i**) and **5i** (Y = CN),^{4d} in addition to the reported derivatives. $\delta(H)$ and $\delta(C)$ of **1–5** were measured carefully in chloroform-*d* solutions (0.050 M) at 297 K.¹¹ Table 1 shows the results. Table 1 also contains $\delta(Se)$ of **1–5** in the solutions under the conditions. $\delta(H)$ and $\delta(C)$ are given from SiMe₄ (TMS), and $\delta(Se)$ are given from MeSeMe for **1a–5a**. Those for **1–5** are given from **1a–5a** (δ_{SCS}), respectively.

$\delta(H)$ are easily affected by the electronic environments around H, in question. They are mainly determined not only by the electron densities but also by the anisotropic effect and charges around the atoms. QC calculations are performed at the density functional theory (DFT) level of the Becke three-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP) of the Gaussian 03 program.^{12–14} Charges at Se and C_i [$Q_n(Se)$ and $Q_n(C_i)$, respectively] are

(11) The 0.050 M CDCl₃ solutions were used for NMR measurements. The concentrations would be lower for the compounds of low solubility, such as **1j** and **2j**, especially at 213 K. However, the concentration dependence of $\delta(H)$ and $\delta(C)$ of **1** and **2** is usually small when they are less than 0.050 M.

(12) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(13) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(14) Frisch, M. J. et al. *Gaussian 03*, revision D.02; Gaussian, Inc.: Wallingford CT, 2004.

calculated with the natural population analysis¹⁵ for **pl** and **pd** of **6a–6j**, to examine the effect of Q_n on $\delta(H)$ and $\delta(C)$ in **pl** and **pd**, with the 6-311+G(3df) basis sets for Se and 6-311+G(3d,2p) basis sets for other nuclei in the Gaussian 03 program.¹⁴ Table 2 shows the results.

Survey of Structures of 1–5 in Solutions Based on $\delta(Se)$. Before discussion of the orientational effect of ArSeR based on $\delta(H)$ and $\delta(C)$, it is instructive to survey the effect employing $\delta(Se)$. The correlation of $\delta(Se)_{SCS}$ of **1** [$\delta(Se: 1)_{SCS}$] versus $\delta(Se: 2)_{SCS}$ is already reported.⁶ The plot of $\delta(Se: 4)_{SCS}$ versus $\delta(Se: 1)_{SCS}$ gave an excellent correlation with the correlation coefficient (r in $y = ax + b$) of 0.9998 (see entry 24 in Table S1 of the Supporting Information (SI)). The plot of $\delta(Se: 5)_{SCS}$ versus $\delta(Se: 2)_{SCS}$ also gave an excellent correlation with $r = 0.9995$, if data of Y = **h–j** are omitted (entry 26 in Table S1 of the SI). These results show that the structure of **4** is (**A: pl**) for all Y examined in the solutions, whereas **5** is (**B: pd**) for Y = **a, c, d, f, and g**. Indeed, **5i** and **5j** are in equilibrium between (**B: pd**) and (**A: pl**) in the solutions, but **5h** is almost in (**B: pd**) because the deviation is small. The plot of $\delta(Se: 3)_{SCS}$ versus $\delta(Se: 1)_{SCS}$ or $\delta(Se: 2)_{SCS}$ could not be analyzed as a linear correlation. As will be discussed later, **3** is in equilibrium

(15) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*, version 3.1.

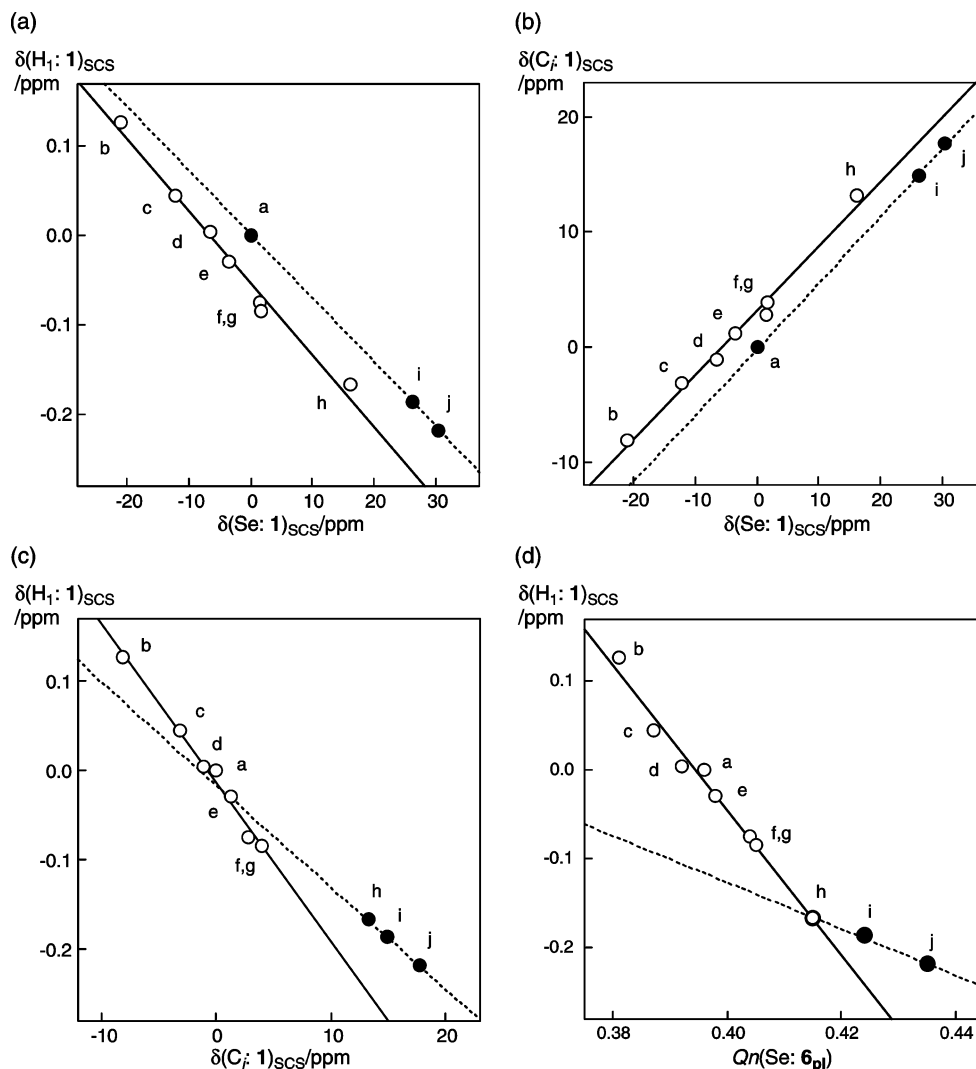


FIGURE 1. Plots in 1: (a) $\delta(\text{H}_1: 1)_{\text{SCS}}$ versus $\delta(\text{Se}: 1)_{\text{SCS}}$; (b) $\delta(\text{C}_i: 1)_{\text{SCS}}$ versus $\delta(\text{Se}: 1)_{\text{SCS}}$; (c) $\delta(\text{H}_1: 1)_{\text{SCS}}$ versus $\delta(\text{C}_i: 1)_{\text{SCS}}$; and (d) $\delta(\text{H}_1: 1)_{\text{SCS}}$ versus $Qn(\text{Se}: 6_{\text{pl}})$.

between (**A: pl**) and (**B: pd**) in the solutions, and the equilibrium constant varies depending on Y.

After a survey of the structures of **1–5** in the solutions based on $\delta(\text{Se})_{\text{SCS}}$, the next extension is to examine the behavior of $\delta(\text{H})_{\text{SCS}}$ and $\delta(\text{C})_{\text{SCS}}$ and the applicability of the values for the structural determination in solutions.

Correlations between $\delta(\text{H})$, $\delta(\text{C})$, and $\delta(\text{Se})$ in **1 (**A: pl**).** To clarify the correlations between $\delta(\text{H})$, $\delta(\text{C})$, and $\delta(\text{Se})$ in **1** (**A: pl**), $\delta(\text{H}_1: 1)_{\text{SCS}}$ and $\delta(\text{C}_i: 1)_{\text{SCS}}$ are plotted versus $\delta(\text{Se}: 1)_{\text{SCS}}$. Figure 1a,b shows the plots. Each plot is analyzed by two correlations. One is shown by a solid line for Y = **b–h** [**G(1: b–h)**], and another is shown by a dotted line for Y = **a, i, and j** [**G(1: a,i,j)**]. All correlations are very good (entries 1–4 in Table S1 of the SI). Similar behavior is observed in the plot of $\delta(\text{H}_1: 1)_{\text{SCS}}$ versus $\delta(\text{C}_i: 1)_{\text{SCS}}$. Figure 1c shows the plot. Data with Y = **b–g** belong to a group [**G(1: b–g)**], and those with Y = **h–j** belong to another group [**G(1: h–j)**], although that of Y = **a** would belong to both. The correlation is very good for each (entries 5 and 6 in Table S1 of the SI).

The plot of $\delta(\text{H}_{10}: 1)_{\text{SCS}}$ versus $\delta(\text{H}_1: 1)_{\text{SCS}}$ is analyzed similarly to the two correlations (see Figure S1a of the SI). The correlation is also very good for each (entries 7 and 8 in Table S1 of the SI). Good correlations are also found in the plots of

$\delta(\text{H}_o: 1)_{\text{SCS}}$, although the data are not shown. The difference of the mechanisms in the transmittance of the substituent effect on $\delta(\text{H})$, $\delta(\text{C})$, and $\delta(\text{Se})$ in **1** must be responsible for the observed double correlations for each.

Why do data for Y = **i, j**, and/or **h** deviate from the correlations? $\delta(\text{H}_1)_{\text{SCS}}$ are plotted versus $Qn(\text{Se}: 6_{\text{pl}})$, where $Qn(\text{Se}: 6_{\text{pl}})$ are used in place of $Qn(\text{Se}: 1)$, as a model. Figure 1d shows the plot. Data for Y = **i** and **j** deviate from the correlation line (entry 9 in Table S1 of the SI), which strongly suggests that the additional contribution of $Qn(\text{Se}: 1)$ to $\delta(\text{H}_1)_{\text{SCS}}$ is responsible for the deviation. These results reconfirm that some deviations in the plot of $\delta(\text{H})_{\text{SCS}}$ and $\delta(\text{C})_{\text{SCS}}$ would occur even if the structure of the system is fixed for all Y examined because the contributions from some mechanisms of the substituent effect to $\delta(\text{H})_{\text{SCS}}$ and $\delta(\text{C})_{\text{SCS}}$ change from position to position in a molecule. Nevertheless, the correlations between $\delta(\text{H}_1)_{\text{SCS}}$, $\delta(\text{C}_i)_{\text{SCS}}$, and $\delta(\text{Se})_{\text{SCS}}$ are good as a whole. Therefore, they can be used for the structural analysis in solutions, if we pay attention to the different contributions from the mechanisms.¹⁶

(16) The deviation of the data for Y = **a** is often observed in such plots; however, the reason is not clear.

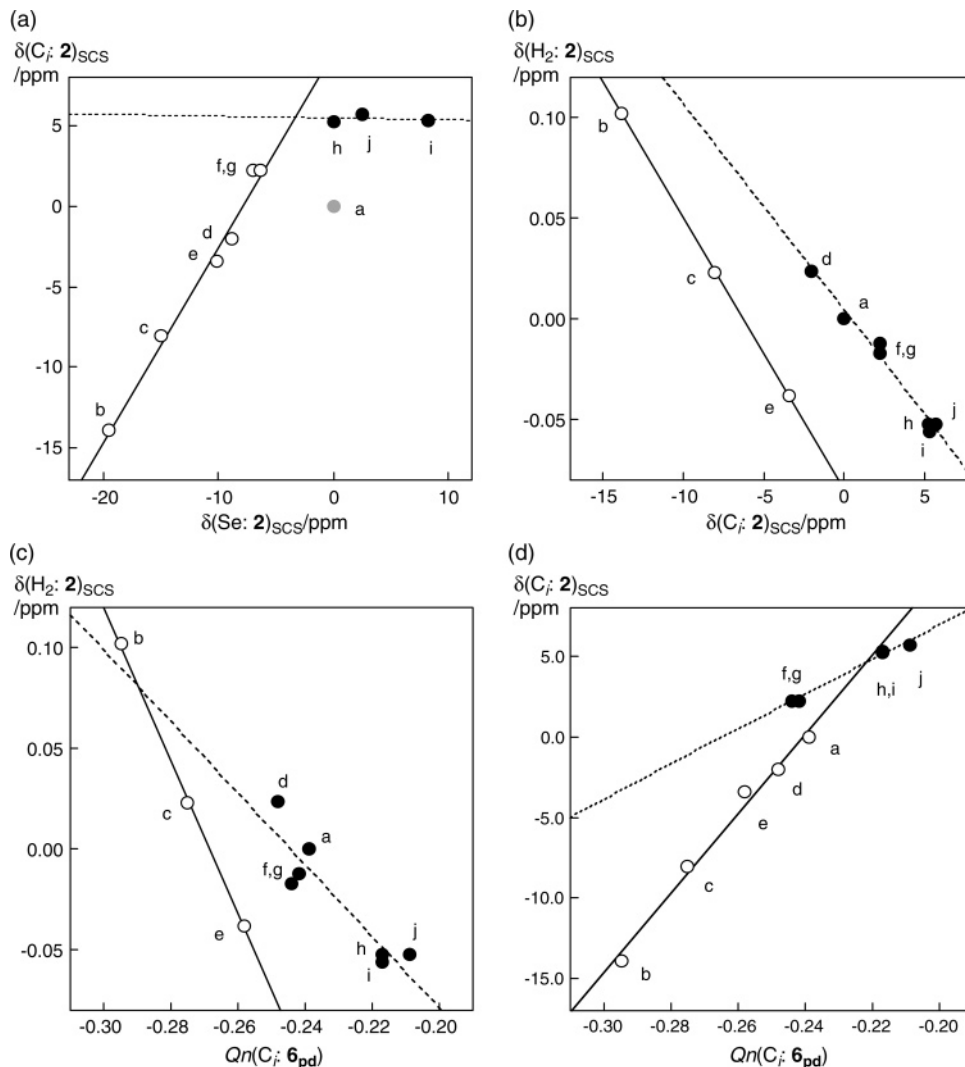


FIGURE 2. Plots in 2: (a) $\delta(C_i: 2)_{SCS}$ versus $\delta(Se: 2)_{SCS}$; (b) $\delta(H_2: 2)_{SCS}$ versus $\delta(C_i: 2)_{SCS}$; (c) $\delta(H_2: 2)_{SCS}$ versus $Qn(C_i: 6_{pd})$; and (d) $\delta(C_i: 2)_{SCS}$ versus $Qn(C_i: 6_{pd})$.

Correlations between $\delta(H)$, $\delta(C)$, and $\delta(Se)$ in 2 (B: pd). $\delta(C_i: 2)_{SCS}$ are plotted versus $\delta(Se: 2)_{SCS}$, of which the structure is (B: pd). Figure 2a shows the plot. The plot is divided into three parts: good correlation is observed for Y = b–g [G(2: b–g)]; $\delta(C_i)_{SCS}$ are almost constant for Y = h–j; and data for Y = a are on neither line (see entries 11 and 12 in Table S1 of the SI for the correlations).

Figure 2b shows the plot of $\delta(H_2: 2)_{SCS}$ versus $\delta(C_i: 2)_{SCS}$. Data for Y = a, d, and f–j make G(2: a,d,f–j), and those for Y = b, c, and e make G(2: b,c,e) (see entries 13 and 14 in Table S1 of the SI for the correlations). Figure 2c shows the plot of $\delta(H_2: 2)_{SCS}$ versus $Qn(C_i: 6_{pd})$, which is analyzed as two correlations with G(2: a,d,f–j) and G(2: b,c,e) (see entries 15 and 16 in Table S1 of the SI for the correlations). Figure 2b,c is closely correlated with each other. The results show that the effect of $Qn(C_i: 2)$ on $\delta(H_2: 2)_{SCS}$ is responsible for the double correlations in the plot of $\delta(H_2: 2)_{SCS}$ versus $\delta(C_i: 2)_{SCS}$. The plot of $\delta(C_i: 2)_{SCS}$ versus $Qn(C_i: 6_{pd})$ gave good correlations (entries 17 and 18 in Table S1 of the SI), as exhibited in Figure 2d, which supports the above expectation. The donating ability of G(2: b,c,e) may also play an important role in the mechanism.

How are $\delta(H_2: 2)_{SCS}$ correlated to $\delta(H_1: 1)_{SCS}$? Figure 3a exhibits the plot, which is analyzed as two correlations (entries 19 and 20 in Table S1 of the SI). The two correlations are also a reflection of the behavior of $\delta(H_2: 2)_{SCS}$ observed in Figure 2c. $\delta(C_i: 2)_{SCS}$ are also plotted versus $\delta(C_i: 1)_{SCS}$. Figure 3b shows the plot. The plot is divided into three parts, similarly to the case of Figure 2a. Although the correlation constant (a in $y = ax + b$) is small for Y = f–j [G(2/1: f–j)], a very good one is obtained for Y = b, c, and e [G(2/1: b,c,e)]. Data for Y = a and d deviate from the correlation lines (see entries 21 and 22 in Table S1 of the SI for the correlations). Figure 3b somewhat resembles Figure 3a.

Scheme 3 summarizes the mechanisms for the transmittance of the substituent effect on $\delta(H)$. Because Y accepts electrons from the phenylselenanyl group or donates them to the group, relative to Y = H, the electron density of the phenyl ring changes. The effects of the anisotropy and charge at Se and/or C on $\delta(H)$ also change depending on Y. The efficiency of the effect on $\delta(H)$ is different from position to position of H even if the structure is fixed for all Y examined. Consequently, plots sometimes do not give good correlations under the conditions.

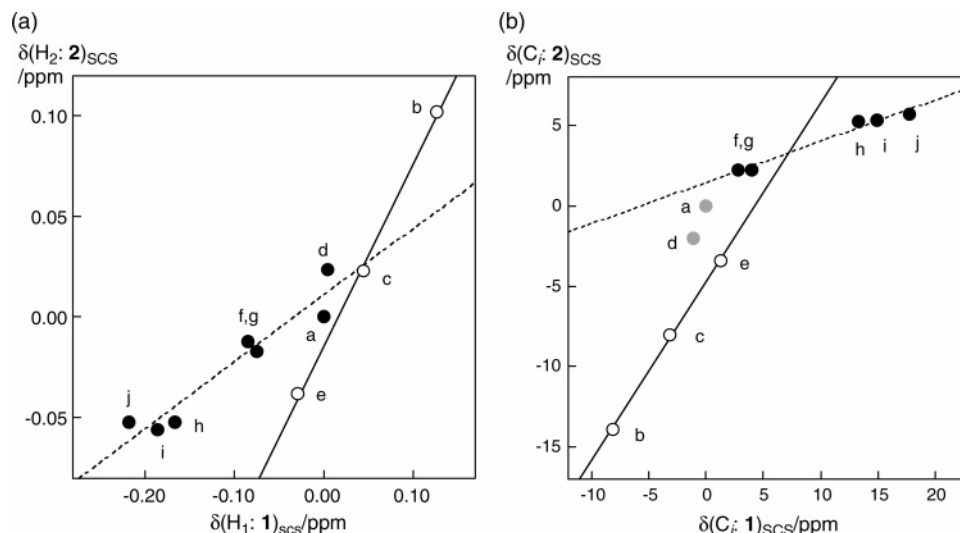
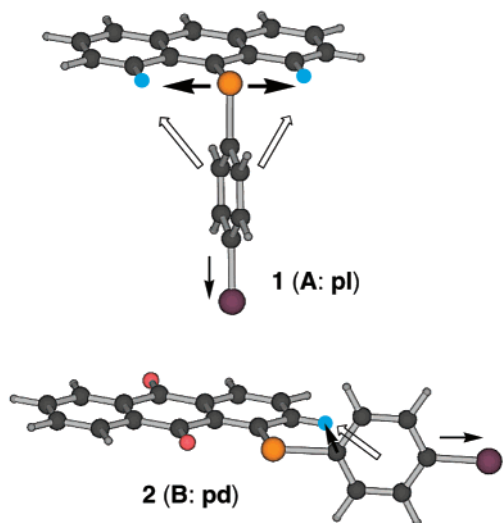


FIGURE 3. Plots in **2** versus **1**: (a) $\delta(\text{H}_2: \mathbf{2})_{\text{SCS}}$ versus $\delta(\text{H}_1: \mathbf{1})_{\text{SCS}}$ and (b) $\delta(\text{C}: \mathbf{2})_{\text{SCS}}$ versus $\delta(\text{C}: \mathbf{1})_{\text{SCS}}$.

SCHEME 3. Effects of Anisotropy and Charge of the Arylselenanyl Group on $\delta(\text{H}_1)$ in **1 (A: **pl**) and on $\delta(\text{H}_2)$ in **2** (B: **pd**)^a**



^a Solid (regular), outlined, and thick arrows stand for electron movement, effects of anisotropy, and charge, respectively. The charge affects mainly from $Qn(\text{Se})$ to $\delta(\text{H}_1)$ in **1** (A: **pl**) and $Qn(\text{C}_i)$ to $\delta(\text{H}_2)$ in **2** (B: **pd**).

$\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$ are demonstrated to be reliable as the standards for **pl** and **pd**, respectively. However, the above results show that we must consider the mechanisms for the transmittance of substituent effect to each position, namely, the reason for deviations in the plots. Good results will be obtained by choosing the positions of $\delta(\text{H})$ and $\delta(\text{C})$ in a molecule in question, when $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$ are used as the standards for the structural analysis in solutions.

After clarifying the behavior of $\delta(\text{H})$, $\delta(\text{C})$, and $\delta(\text{Se})$ in **1** (A: **pl**) and **2** (B: **pd**), the next extension is to apply $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$ to determine the structures in the solutions. Before discussion of the structure of **3**, it is practical to clarify the structures of **4** and **5** in the solutions, first.

Structure of **4 in Solutions.** How is the structure of **4** determined on the basis of $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$ in solutions? $\delta(\text{H}_8: \mathbf{4})_{\text{SCS}}$ are plotted versus $\delta(\text{H}_1: \mathbf{1})_{\text{SCS}}$. Figure 4a shows the plot. The correlation is very good (entry 23 in

Table S1 of the SI). The results exhibit that the structure of **4** is (A: **pl**) for all Y examined in the solution, similarly to the case of **1** (A: **pl**) (see Scheme 2). The methyl group at the 2-position of **4** must sterically prevent the structure from being **B**.¹⁷ $\delta(\text{Se}: \mathbf{4})_{\text{SCS}}$ are also plotted versus $\delta(\text{Se}: \mathbf{1})_{\text{SCS}}$, which is shown in Figure 4b. The correlation is also excellent (entry 24 in Table S1 of the SI). The results of $\delta(\text{H}_8: \mathbf{4})_{\text{SCS}}$ are perfectly supported by those of $\delta(\text{Se}: \mathbf{4})_{\text{SCS}}$. Consequently, it is confirmed again that $\delta(\text{H}_1: \mathbf{1})_{\text{SCS}}$ can be used as the practical standard to determine the structures of aryl selenides in solutions, in relation to the orientational effect.

Structure of **5 in Solution.** What is the structure of **5** in solutions? $\delta(\text{H}_2: \mathbf{5})_{\text{SCS}}$ are plotted versus $\delta(\text{H}_2: \mathbf{2})_{\text{SCS}}$. A fairly good correlation was obtained except for data with Y = **i** and **j**, which apparently deviate from the correlation line. Figure 5a shows the results (entry 25 in Table S1 of the SI). These results exhibit that the structure of **5** is (B: **pd**) in the solutions, except for Y = **i** and **j**. **5i** and **5j** must be substantially in equilibrium between (B: **pd**) and (A: **pl**) in the solutions. Y of electron-withdrawing groups prefer (A: **pl**) due to the p- π conjugation.^{3d} The energy lowering effect by the $n_p(\text{Br})\text{---}\sigma^*(\text{Se}-\text{C})$ 3c-4e in **5** would not be large enough to keep the structure (B: **pd**), overwhelming the p- π conjugation, for Y = **i** and **j**. On the other hand, the $n_p(\text{O})\text{---}\sigma^*(\text{Se}-\text{C})$ 3c-4e in **2** is strong enough to maintain the structure (B: **pd**) for all Y examined. The through π interaction of the $\pi(\text{C}=\text{O})\text{---}\pi(\text{Ar})\text{---}p(\text{Se})$ type also operates to stabilize **2** (B: **pd**). Scheme 4 explains the factors to stabilize (B: **pd**).

Very similar behavior is observed in the plot of $\delta(\text{Se}: \mathbf{5})_{\text{SCS}}$ versus $\delta(\text{Se}: \mathbf{2})_{\text{SCS}}$. The plot is shown in Figure 5b (see entry 26 in Table S1 of the SI for the correlation). Data with Y = **i** and **j** apparently deviate again from the correlation line. The slight deviation from the line is also observed for the data of Y = **h**. The conclusion obtained based on $\delta(\text{H}_2: \mathbf{2})_{\text{SCS}}$ is well supported by that based on $\delta(\text{Se}: \mathbf{2})_{\text{SCS}}$. The observation of the slight deviation in $\delta(\text{Se}: \mathbf{5h})_{\text{SCS}}$ must come from the higher accuracy in the plot of $\delta(\text{Se}: \mathbf{5})_{\text{SCS}}$. The width in $\delta(\text{H}_2: \mathbf{2})_{\text{SCS}}$

(17) A good correlation is also expected for the plot of $\delta(\text{H}_{\text{Me}}: \mathbf{4})_{\text{SCS}}$ versus $\delta(\text{H}_1: \mathbf{1})_{\text{SCS}}$. However, the correlation is very poor (see Figure S1b in the SI). The magnitudes of $\delta(\text{H}_{\text{Me}}: \mathbf{4})_{\text{SCS}}$ are very small, relative to $\delta(\text{H}_8: \mathbf{4})_{\text{SCS}}$, which must be responsible for the poor correlation.

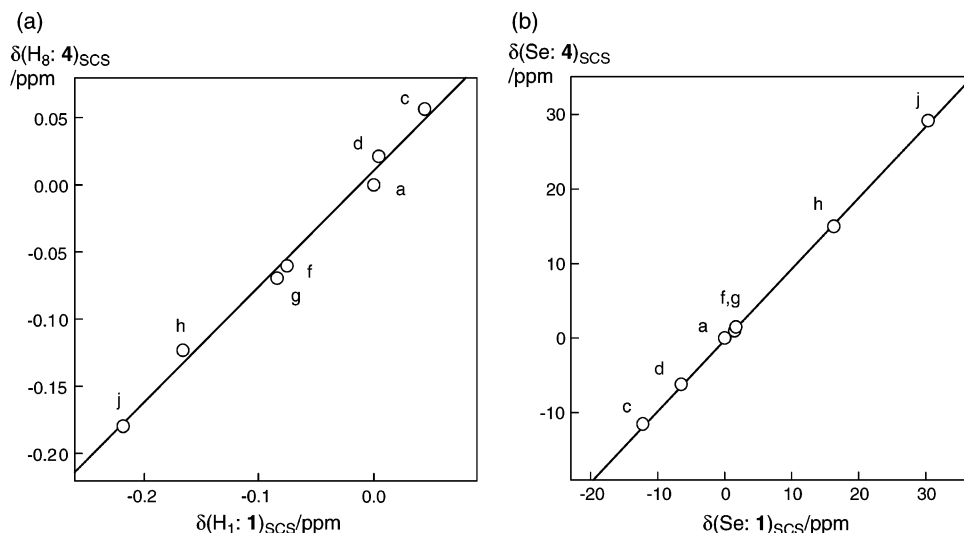


FIGURE 4. Plots in 4 versus 1: (a) $\delta(H_8: 4)_{SCS}$ versus $\delta(H_1: 1)_{SCS}$ and (b) $\delta(Se: 4)_{SCS}$ versus $\delta(Se: 1)_{SCS}$.

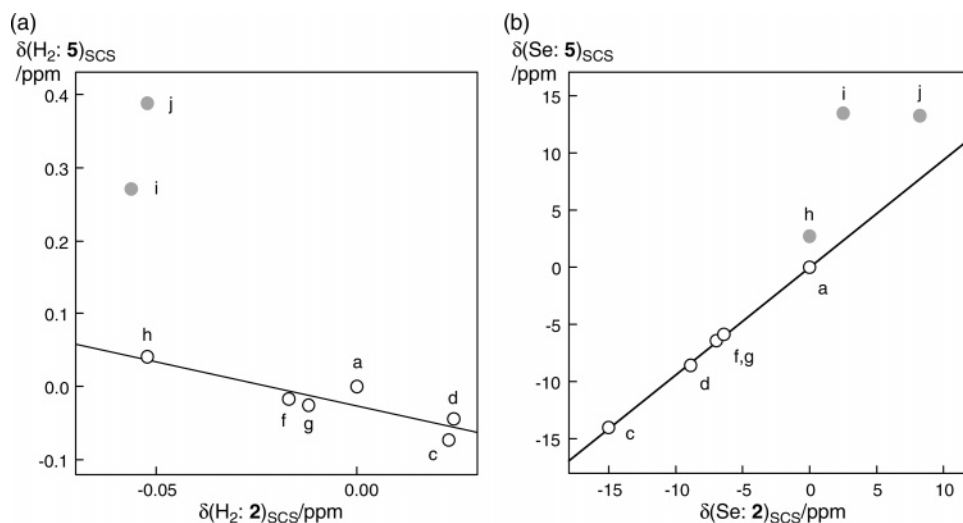
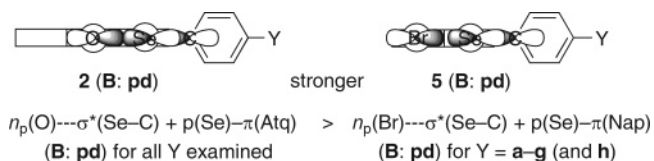


FIGURE 5. Plots in 5: (a) $\delta(H_2: 5)_{SCS}$ versus $\delta(H_2: 2)_{SCS}$ and (b) $\delta(Se: 5)_{SCS}$ versus $\delta(Se: 2)_{SCS}$.

SCHEME 4. Factors to Control the Structures of 2 and 5 to be (B: pd)



(ca. 0.15 ppm) is much smaller than that in $\delta(Se: 2)_{SCS}$ (ca. 28 ppm). A smaller width will produce a larger error in the plot and vice versa. Although not shown, very similar results are obtained in 1-(arylselenanyl)-8-chloronaphthalenes [1-(*p*-YC₆H₄-Se)NapCl-8].

These results demonstrate that $\delta(H_2: 2)_{SCS}$ can be used to analyze the structures of aryl selenides in the solution, in relation to the orientational effect.

After examination of the applicability of $\delta(H)$ and $\delta(C)$ of 1 and 2, exemplified by 4 and 5, the next extension is to clarify the structure of 3 in the solutions, by employing $\delta(H)$ and $\delta(C)$ of 1 and 2.

Structure of 3 in Solutions. How is the structure of 3 analyzed in solutions? $\delta(H_2: 3)_{SCS}$ are plotted versus $\delta(H_1: 1)_{SCS}$.

Figure 6a exhibits the plot, which is analyzed as a parabolic curve. The results show that 3 is in equilibrium between (A: pl) and (B: pd) in the solutions, and the equilibrium constant varies depending on Y. Figure 6b shows the plot of $\delta(Se: 3)_{SCS}$ versus $\delta(Se: 1)_{SCS}$. The plot is analyzed as an S-shaped correlation. The results also support the conclusion obtained in the plot of $\delta(H_2: 3)_{SCS}$ versus $\delta(H_1: 1)_{SCS}$.

$\delta(H_8: 3)_{SCS}$ are plotted versus $\delta(H_1: 1)_{SCS}$, next. Figure 6c shows the results. The plots are analyzed as two correlations (entries 27 and 28 in Table S1 of the SI).¹⁸ Figure 6c can be explained by assuming that the structure of 3 is mainly (B: pd) for Y of strong donors, such as Y = b, c, and e, whereas it is essentially (A: pl) for Y of accepting groups such as Y = f–j. The structure is substantially in equilibrium between (A: pl) and (B: pd) in the solutions for Y of electronically intermediate ability. Figure 6c could be explained by the roof-type correlation starting from Y = b, c, e–j. In this case, data with Y = a and

(18) The plot of $\delta(C: 3)_{SCS}$ versus $\delta(C: 1)_{SCS}$ is also analyzed as two correlations: $y = 1.300x - 7.538$ ($r = 0.9999$) for Y = b, c, and e, and $y = 0.901x - 3.831$ ($r = 0.999$) for Y = d, f–j, although data for Y = a deviate the line.

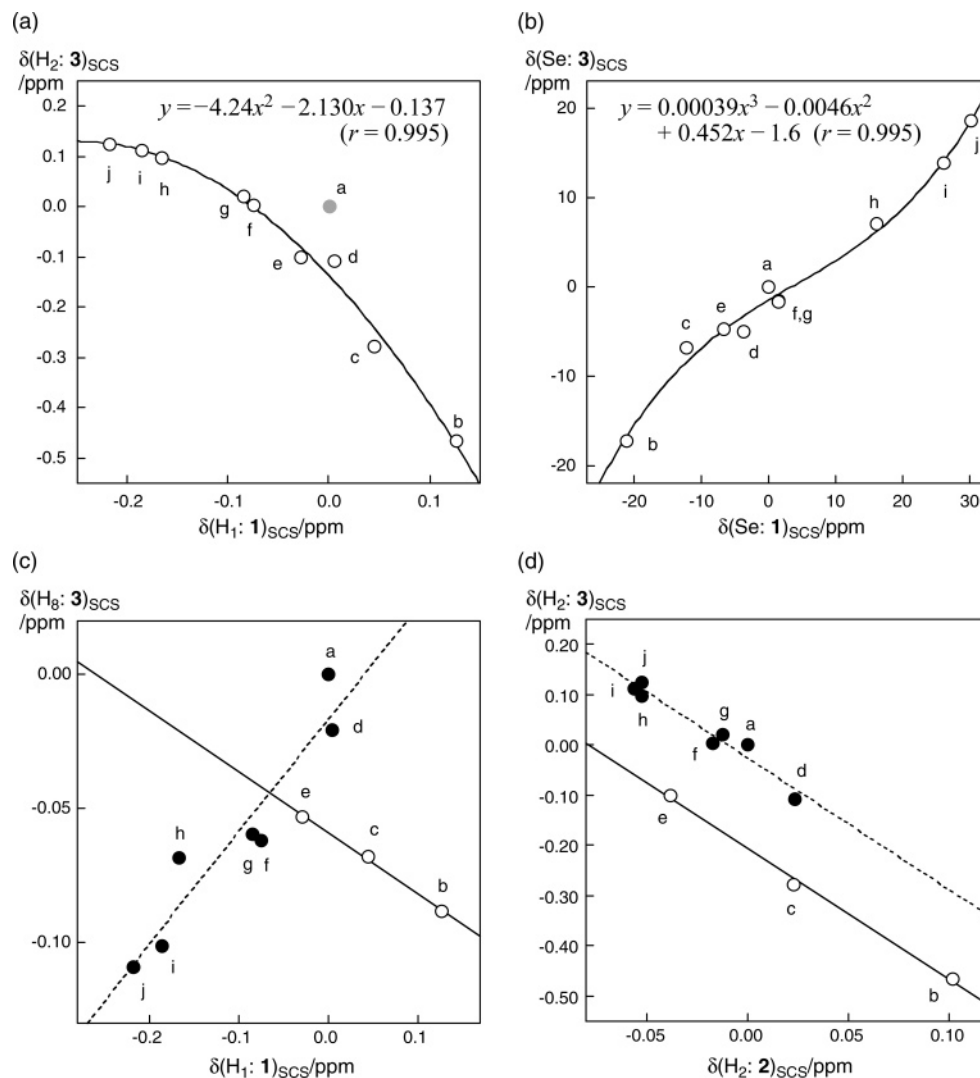


FIGURE 6. Plots in **3**: (a) $\delta(\text{H}_2: \mathbf{3})_{\text{SCS}}$ versus $\delta(\text{H}_1: \mathbf{1})_{\text{SCS}}$; (b) $\delta(\text{Se}: \mathbf{3})_{\text{SCS}}$ versus $\delta(\text{Se}: \mathbf{1})_{\text{SCS}}$; (c) $\delta(\text{H}_8: \mathbf{3})_{\text{SCS}}$ versus $\delta(\text{H}_1: \mathbf{1})_{\text{SCS}}$; and (d) $\delta(\text{H}_2: \mathbf{3})_{\text{SCS}}$ versus $\delta(\text{H}_2: \mathbf{2})_{\text{SCS}}$.

d seem to deviate from the roof correlation. As shown in Figure 6d, the plot of $\delta(\text{H}_2: \mathbf{3})_{\text{SCS}}$ versus $\delta(\text{H}_2: \mathbf{2})_{\text{SCS}}$ is similarly analyzed as two correlations (entries 29 and 30 in Table S1 of the SI). The results are inconsistent with the assumption that the structure of **3** is mainly (A: **pl**) for Y of accepting groups. The behavior for Y of strong donors is complex when analyzed by $\delta(\text{H}_2: \mathbf{2})_{\text{SCS}}$. These results demonstrate that the combination of $\delta(\text{H}: \mathbf{1})_{\text{SCS}}$ and $\delta(\text{H}: \mathbf{2})_{\text{SCS}}$ can be a more powerful tool as a standard to analyze the structures in solutions, if they are applied carefully.

Equilibrium constants between **3** (A: **pl**) and **3** (B: **pd**) in solutions are considered, next. Structures of **3a**, **3b**, and **3j** in the (A: **pl**) and (B: **pd**) conformers were optimized with the B3LYP/6-311+G(d,p) method of the Gaussian 03 program,¹⁴ and the solvent effect of chloroform was calculated for the compounds with the IPCM¹⁹ method, employing the B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) method. Table 3 shows the results, containing the solvent effect of chloroform. The thermal effect based on the frequency analysis is also shown for **3b**.

TABLE 3. Calculated Energies of **3** (A: **pl**) and **3** (B: **pd**) for Y = a, b, and j^a

| compd | 3b | 3a | 3j |
|--|------------|-------------------|------------|
| $E(\text{type A})$ (au) | -3152.6380 | -3018.6354 | -3223.2004 |
| $E(\text{type B})$ (au) | -3152.6400 | -3018.6350 | -3223.1962 |
| ΔE^b (kJ/mol) | 5.3 | -1.1 ^c | -11.0 |
| containing the solvent effect of chloroform ^d | | | |
| $E(\text{type A})$ (au) | -3152.6449 | -3018.6405 | -3223.2195 |
| $E(\text{type B})$ (au) | -3152.6563 | -3018.6438 | -3223.2033 |
| ΔE^b (kJ/mol) | 29.9 | 8.7 | -42.5 |

^a Calculated with the B3LYP/6-311+G(d,p) method. ^b $\Delta E = E(\text{type A}) - E(\text{type B})$. ^c The value with the thermal effect is almost equal to that on the potential energy surface. ^d Calculated with the IPCM method.¹⁹

The evaluated ΔE values [$E(\text{type A}) - E(\text{type B})$] for **3b** and **3j** are 30 and -43 kJ/mol, respectively. The values predict over 99.9% for (B: **pd**) and over 99.9% (A: **pl**) for **3b** and **3j**, respectively. Compilation of these results led us to a conclusion that the structures of **3b** and **3j** are predominantly (B: **pd**) and (A: **pl**), respectively, and **3** with Y of electronically intermediate ability is substantially in equilibrium between the two structures in the solutions judging from the ΔE of 9 kJ/mol for **3a**.

(19) Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch, M. J. *J. Phys. Chem.* **1996**, *100*, 16098–16104.

Conclusion

We have pointed out the importance of the orientational effect on $\delta(\text{Se})$ of $p\text{-YC}_6\text{H}_4\text{SeR}$ (ArSeR), for the better structural analysis in solutions based on the chemical shifts. Two sets of $\delta(\text{H})$ and $\delta(\text{C})$ are proposed for each **1** [$9\text{-}(p\text{-YC}_6\text{H}_4\text{Se})\text{Atc}$] and **2** [$1\text{-}(p\text{-YC}_6\text{H}_4\text{Se})\text{Atq}$], where $\text{Y} = \text{H}$ (**a**), NMe_2 (**b**), OMe (**c**), Me (**d**), F (**e**), Cl (**f**), Br (**g**), COOEt (**h**), CN (**i**), and NO_2 (**j**) to analyze the structures of $p\text{-YC}_6\text{H}_4\text{SeR}$ (ArSeR) in solutions based on $\delta(\text{H})$ and $\delta(\text{C})$, together with $\delta(\text{Se})$. The structures of **1** and **2** are (**A**: **pl**) and (**B**: **pd**), respectively, for all Y examined in chloroform-*d* solutions. $\delta(\text{H}: \mathbf{1})$ and $\delta(\text{C}: \mathbf{1})$ are typical for (**A**: **pl**), and $\delta(\text{H}: \mathbf{2})$ and $\delta(\text{C}: \mathbf{2})$ are characteristic for (**B**: **pd**).

Indeed, $\delta(\text{H})$ and $\delta(\text{C})$ are widely applied to determine the structures, but it is necessary to clarify the behavior of $\delta(\text{H})$ and $\delta(\text{C})$ for **1** (**A**: **pl**) and **2** (**B**: **pd**) first, for the discussion on the firm basis in relation to the orientational effect. The efficiency of the electronic and anisotropic effects (mechanisms for the transmittance of the substituent effect) changes from position *a* to position *b*. Therefore, the behavior of $\delta(\text{H})$ at position *a* [$\delta(\text{H}_a)$] sometimes does not correlate well with $\delta(\text{H}_b)$, even if the structures are fixed for all Y examined. Consequently, it is necessary to select suitable positions of $\delta(\text{H})$ and $\delta(\text{C})$ in a molecule in question for the better correlations when $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$ are used as the standards for the structural analysis in solutions.

Structures are analyzed for **3** [$1\text{-}(p\text{-YC}_6\text{H}_4\text{Se})\text{Nap}$], **4** [$1\text{-}(p\text{-YC}_6\text{H}_4\text{Se})\text{NapMe-2}$], and **5** [$1\text{-}(p\text{-YC}_6\text{H}_4\text{Se})\text{NapBr-8}$] in the chloroform-*d* solutions, by employing $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$, after the elucidation of the behavior of $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$. Although the structure of **4** remains in (**A**: **pl**) in the solutions, for all Y examined, that of **5** is (**B**: **pd**) in the solutions, except for $\text{Y} = \text{i}$ and **j**. Although **5j** and **5i** are substantially in equilibrium between (**B**: **pd**) and (**A**: **pl**) in the solutions, **5h** exists almost predominantly in (**B**: **pd**). Very similar results are obtained for 1-(arylselanyl)-8-chloronaphthalenes. The energy lowering effect of the $n_p(\text{X})\text{---}\sigma^*(\text{Se}\text{---}\text{C})\text{3c}\text{---}4\text{e}$ ($\text{X} = \text{Br}$ in **5**) seems not to be large enough to keep the structure (**B**: **pd**) for $\text{Y} = \text{i}$ and **j**, whereas the $n_p(\text{O})\text{---}\sigma^*(\text{Se}\text{---}\text{C})\text{3c}\text{---}4\text{e}$ in **2** is strong enough for all Y examined. In the case of **3**, the structure is demonstrated to equilibrate between (**A**: **pl**) and (**B**: **pd**), and the equilibrium constants change from Y to Y in the solutions. Meanwhile, the contributions of (**B**: **pd**) and (**A**: **pl**) are shown to be predominant for **3b** and **3j**, respectively, based on the QC calculations containing the solvent effect of chloroform. $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$, as well as $\delta(\text{Se})$, are demonstrated to be powerful tools as the standards to analyze the structures of $p\text{-YC}_6\text{H}_4\text{SeR}$ in solutions, if they are applied carefully.

Further investigations on the orientational effect, containing the applications of $\delta(\text{H}, \text{C}: \mathbf{1})$ and $\delta(\text{H}, \text{C}: \mathbf{2})$ to the structural analysis of $p\text{-YC}_6\text{H}_4\text{ZR}$ ($\text{Z} = \text{S}, \text{Te}, \text{and O}$), are in progress aiming to clarify the whole picture of the effect. The results will be reported elsewhere.

Experimental

General. NMR spectra were recorded at 24 °C on a spectrometer (^1H , 300 MHz; ^{13}C , 75.45 MHz; ^{77}Se , 57.25 MHz). The ^1H , ^{13}C , and ^{77}Se chemical shifts are given in parts per million relative to those of Me_4Si , internal CDCl_3 in the solvent, and external MeSeMe , respectively.

1a–1j and **2a–2j** were prepared according to the reported methods.^{3d,6,20} ^1H , ^{13}C , and ^{77}Se NMR chemical shifts of the compounds rationalize the structures. Experimental procedures and analytical/spectroscopic data for **3b**, **3e**, **3i**, **4c**, **4d–j**, and **5i** are shown in the Supporting Information section.

1-(Phenylselanyl)-2-methylnaphthalene (4a). Under an argon atmosphere, an ether solution of diphenyl diselenobromide (3.51 g, 11.3 mmol) was added to Grignard reagent prepared from 1-bromo-2-methylnaphthalene²¹ (2.50 g, 11.3 mmol) and magnesium (0.35 g, 14.7 mmol) in 70 mL of dry ether. Then the solution was refluxed for 2 h, and 20 mL of 5% hydrochloric acid was added. The solution was extracted with 100 mL of benzene. The organic layer was separated and washed with brine, a 10% aqueous solution of sodium hydroxide, a saturated aqueous solution of sodium bicarbonate, and brine. Then the solution was dried over sodium sulfate, evaporated, and dried in vacuo. The crude product was purified by column chromatography (SiO_2 , hexane). **4a** was isolated in 68% yield as pale yellow oil: ^1H NMR (300 MHz, CDCl_3/TMS) δ 2.71 (s, 3H), 7.06–7.10 (m, 5H), 7.43 (dt, $J = 1.4$ and 7.0 Hz, 1H), 7.46 (dd, $J = 1.4$ and 8.3 Hz, 1H), 7.48 (dt, $J = 1.6$ and 7.8 Hz, 1H), 7.81 (dd, $J = 1.8$ and 7.8 Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 8.59 (ddd, $J = 0.8, 2.0,$ and 7.9 Hz, 1H); ^{77}Se NMR (57.25 MHz, $\text{CDCl}_3/\text{MeSeMe}$) δ 274.6. Elemental anal. calcd (%) for $\text{C}_{17}\text{H}_{14}\text{Se}$: C, 68.69; H, 4.75. Found: C, 68.72; H, 4.68.

Bis(2,2'-methylnaphthyl)-1,1'-diselenide (7). Under an argon atmosphere, selenium powder (3.55 g, 45 mmol) was put in Grignard reagent prepared from 1-bromo-2-methylnaphthalene²¹ (10.0 g, 45 mmol) and magnesium (1.42 g, 59 mmol) in 150 mL of dry ether at 4–5 °C. Then the suspension was refluxed for 2 h and was oxidized by air overnight, and 20 mL of 5% hydrochloric acid was added. The solution was extracted with an additional 100 mL of benzene. The organic layer was washed with a 10% aqueous solution of sodium hydroxide, a saturated aqueous solution of sodium bicarbonate, and water. The solution was dried with calcium chloride, evaporated, and dried in vacuo. The crude was recrystallized from hexane. **7** was isolated in 74% yield as orange needles: mp 120.8–121.6 °C; ^1H NMR (300 MHz, CDCl_3/TMS) δ 2.27 (s, 3H), 7.18 (d, $J = 8.6$ Hz, 2H), 7.19 (t, $J = 7.7$ Hz, 2H), 7.34 (t, $J = 7.6$ Hz, 2H), 7.69 (d, $J = 8.5$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 8.14 (d, $J = 7.7$ Hz, 2H). Elemental anal. calcd (%) for $\text{C}_{22}\text{H}_{18}\text{Se}_2$: C, 60.01; H, 4.12. Found: C, 60.07; H, 4.00.

QC Calculations. QC calculations were performed on **6a–6j** in **pl** and **pd** conformations with the 6-311+G(3df) basis sets for Se and the 6-311+G(3d,2p) basis sets for other nuclei of the Gaussian 03 program.¹⁴ Calculations were performed at the density functional theory (DFT) level of the Becke three-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP).^{12,13} Charges were calculated by the natural population analysis.¹⁵ Structures of **3a**, **3b**, and **3j** in types **A** and **B** were optimized with the B3LYP/6-311+G(d,p) method and the solvent effect of chloroform with the IPCM¹⁹ method, employing the B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) method.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research (Nos. 16550038 and 19550041) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

(20) Nakanishi, W.; Hayashi, S.; Itoh, N. *J. Org. Chem.* **2004**, *69*, 1676–1684.

(21) Adams, R.; Binder, L. O. *J. Am. Chem. Soc.* **1941**, *63*, 2773–2776.

(22) The contribution of relativistic terms has been pointed out for heavier atoms, but the perturbation would be small for the selenium nucleus. See: Fukuda, R.; Hada, M.; Nakatsuji, H. *J. Chem. Phys.* **2003**, *118*, 1015–1026. Fukuda, R.; Hada, M.; Nakatsuji, H. *J. Chem. Phys.* **2003**, *118*, 1027–1035. Tanaka, S.; Sugimoto, M.; Takashima, H.; Hada, M.; Nakatsuji, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 953–959. Ballard, C. C.; Hada, M.; Kaneko, H.; Nakatsuji, H. *Chem. Phys. Lett.* **1996**, *254*, 170–178. Nakatsuji, H.; Hada, M.; Kaneko, H.; Ballard, C. C. *Chem. Phys. Lett.* **1996**, *255*, 195–202. Hada, M.; Kaneko, H.; Nakatsuji, H. *Chem. Phys. Lett.* **1996**, *261*, 7–12.

Supporting Information Available: Correlations between δ -(H)_{SCS}, δ (C)_{SCS}, and δ (Se)_{SCS} in **1–5**; plots of δ (H₁₀: **1**)_{SCS} versus δ (H₁: **1**)_{SCS} and δ (H_{Me}: **4**)_{SCS} versus δ (H₁: **1**)_{SCS}; general considerations in experiment; experimental procedures and analytical/spectroscopic data for **3b**, **3e**, **3i**, **4c**, **4d–j**, and **5i**; complete

ref 14; optimized structures given by Cartesian coordinates for **6a–j** in **pl** and **pd** and **3a**, **3b**, and **3j** in types **A** and **B** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO070988G